Development of metal-based electrodes for non-aqueous redox flow batteries

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ABSTRACT

The electrochemistry of a non-aqueous redox flow battery employing nickel and iron bipyridine in tetraethylammonium tetrafluoroborate and propylene carbonate has been investigated. $Ni(0)/Ni(II)$ and $Fe(II)/Fe(III)$ redox couples showed reversible reactions for negative and positive electrodes, respectively. Various metal electrodes (Pt, Ir, Ni, Cu, Mo, W, Nb, Co, and Ti) were evaluated for those couples using cyclic voltammetry. Based on the analysis of the cyclic voltammograms, the reactivity and kinetics for the electrochemical reaction of metal complexes were found to strongly depend on the type of metal electrodes. Among non-precious metals, Cu and Mo showed relatively better electrocatalytic activities as negative electrodes for the $Ni(0)/Ni(II)$ redox couple and Ni was the best material as a positive electrode for the $Fe(II)/Fe(III)$ redox couple in terms of electrochemical reactivity and reaction kinetics.

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1. Introduction

Global energy demands for renewable energy are increasing due to the limited supply of fossil fuels and the greenhouse effect of CO_2. For a stable electricity supply from intermittent energy delivery systems such as solar cells and wind turbines, the development of large-scale energy storage systems is of great importance. Recently, redox flow batteries (RFBs) have attracted much attention owing to several advantages of large capacity, low operating temperature, long cycle life, etc [1]. RFBs store and convert electrical energy using surface redox reactions on negative and positive electrodes, which are separated in each electrolyte by an ion exchange membrane. Since the concept of the RFB was first proposed by Thaller [2], various types of RFB system have been developed, which are iron–chromium [2], all-vanadium [3], bromine-polysulfide [4], and vanadium–bromine [5] RFBs using aqueous electrolytes. Energy density of such aqueous RFBs is limited by the electrochemical stability window of water (1.23 V).

Since the energy density of batteries is determined by cell potential and total charge, non-aqueous (organic) electrolytes which have wide potential windows could offer higher energy density than aqueous electrolytes. The electrochemical properties of several metal complexes with organic ligands have been investigated for RFB chemistries [6–11]. Some complexes such as Ru, Fe, U, V, and Cr with acetylacetone (acac) and 2,2′-bipyridine (bpy) as ligands were employed as active species for redox reactions in non-aqueous electrolytes. For those surface redox reactions, Pt and glassy carbon were usually used as electrode materials

to confirm the electrochemical reversibility of the metal complexes. However, the high cost has limited their commercial attractiveness for non-aqueous RFBs. Therefore, cheap and reliable electrode materials should be also exploited.

In this paper, a non-aqueous RFB was constructed of $[Ni(bpy)_3]/[Ni(bpy)_3]^{2+}$ as a negative redox couple and $[Fe(bpy)_3]^{2+}/[Fe(bpy)_3]^{3+}$ as a positive redox couple in propylene carbonate solution. The electrocatalytic activities of various metal electrodes for those couples have been evaluated using cyclic voltammetry.

2. Experimental

The negative electrolyte was prepared by dissolving 0.1 M tris(2,2′-bipyridine) nickel tetrafluoroborate, $[Ni(bpy)_3](BF_4)_2$ (HANCHEM) and 0.5 M tetraethylammonium tetrafluoroborate ($TEABF_4$, HANCHEM) as a supporting electrolyte in propylene carbonate solution (PC, PANAX ETEC). For the positive electrolyte, 0.2 M tris(2,2′-bipyridine) iron tetrafluoroborate, $[Fe(bpy)_3](BF_4)_2$ (HANCHEM) was used with the same supporting electrolyte in the PC solution. Metal foils of Pt, Ir, Ni, Cu, Mo, W, Nb, Co, and Ti were purchased from Alfa Aesar (>99.5%). Cyclic voltammetry (CV) measurements were carried out using a potentiostat/galvanostat (EC-Lab, BioLogic) in a three-electrode glass cell, consisting of a metal foil (working electrode), a Pt mesh (counter electrode), and an Ag/Ag^+ reference electrode at various scan rates.

3. Results and discussion

Fig. 1 shows the cyclic voltammograms (CV) of various metal electrodes measured at a scan rate of 10 mV s^{-1} in 0.1 M $[Ni(bpy)_3](BF_4)_2$/0.5 M $TEABF_4$ in PC solution. For each electrode, a cathodic peak at around 1.9 V and an anodic peak at approximately 1.5 V vs.

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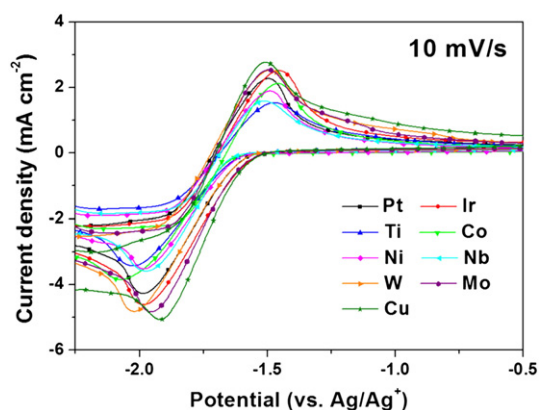E-mail addresses: kijaekim@keti.re.kr (K.J. Kim), yjkim@keti.re.kr (Y.-J. Kim).

Fig. 1. Cyclic voltammograms of various metal electrodes for the $[Ni(bpy)_3]/[Ni(bpy)_3]^{2+}$ couple at a scan rate of 10 mV s^{-1}.

Ag/Ag$^+$ were observed. As reported in the literature [12,13], the peaks are associated with the reduction and oxidation reactions of [Ni(bpy)$_3$]/[Ni(bpy)$_3$]$^{2+}$ couple as follows:

$$[Ni(bpy)_3]^{2+} + 2e^- = Ni(bpy)_3 \qquad (1)$$

At the scan rate of 10 mV s^{-1}, some metals such as Cu, Mo, Pt, Ir, and W are found to be providing relatively better reactivity as catalysts for the oxidation reaction, indicating that the metals can be working as negative electrodes to produce higher discharge current during full cell operations.

In order to investigate the kinetics of the redox reaction, the CV curves of Cu, Mo, and Pt, which showed relatively high anodic currents, at various scan rates are compared in Fig. 2. For each electrode, the peak separation between cathodic and anodic scans is getting bigger when the scan rate is increased. This phenomenon is usually observed in CV measurements for an electrochemical process because more overpotential is required for the reduction and oxidation reactions, which is resulted from (1) potential drop by slow electronic or ionic transport; (2) sluggish charge transfer on the electrode/electrolyte interface. In a cyclic voltammogram, the scan-rate dependence of the response current for a simple process can be distinguished whether the process is controlled by a surface reaction (linear dependence, $i \propto \upsilon$; i = current, υ = scan rate) or a diffusion-limited mechanism (square-root dependence, $i \propto \upsilon^{1/2}$). And a mixed process of both can also exist. The relation of the anodic peak current of the metal electrodes and the scan rate is plotted in Fig. 2(d) to examine the scan-rate dependence on the redox reaction of the [Ni(bpy)$_3$]/[Ni(bpy)$_3$]$^{2+}$ couple. For all samples, the linear dependence is observed up to 5 mV s^{-1}, the deviation from which begins to appear at 10 mV s^{-1}. From this point, the anodic current might be limited by surface charge transfer and/or ionic transport in the electrolyte but the relation was neither the square-root dependence nor the mixed process. Overall, the rate performances of Pt and Mo are slightly better than that of Cu while Cu shows a little higher current density. Based on the electrochemical evaluation of anodic current values and scan-rate dependence, except noble metals, it is found that Cu and Mo are promising candidates as negative electrodes for the Ni bipyridine couple in non-aqueous RFBs.

Fig. 3 presents the CVs of various metal electrodes at a scan rate of 10 mV s^{-1} in 0.1 M [Fe(bpy)$_3$](BF$_4$)$_2$/0.5 M TEABF$_4$ in PC solution. The features of the CV shapes were classified into three groups. For Pt, Ir, and Ni electrodes, the CV curves clearly show a pair of anodic and cathodic peaks at approximately 0.8 and 0.4 V vs. Ag/Ag$^+$, respectively. The peaks correspond to the oxidation and reduction reactions
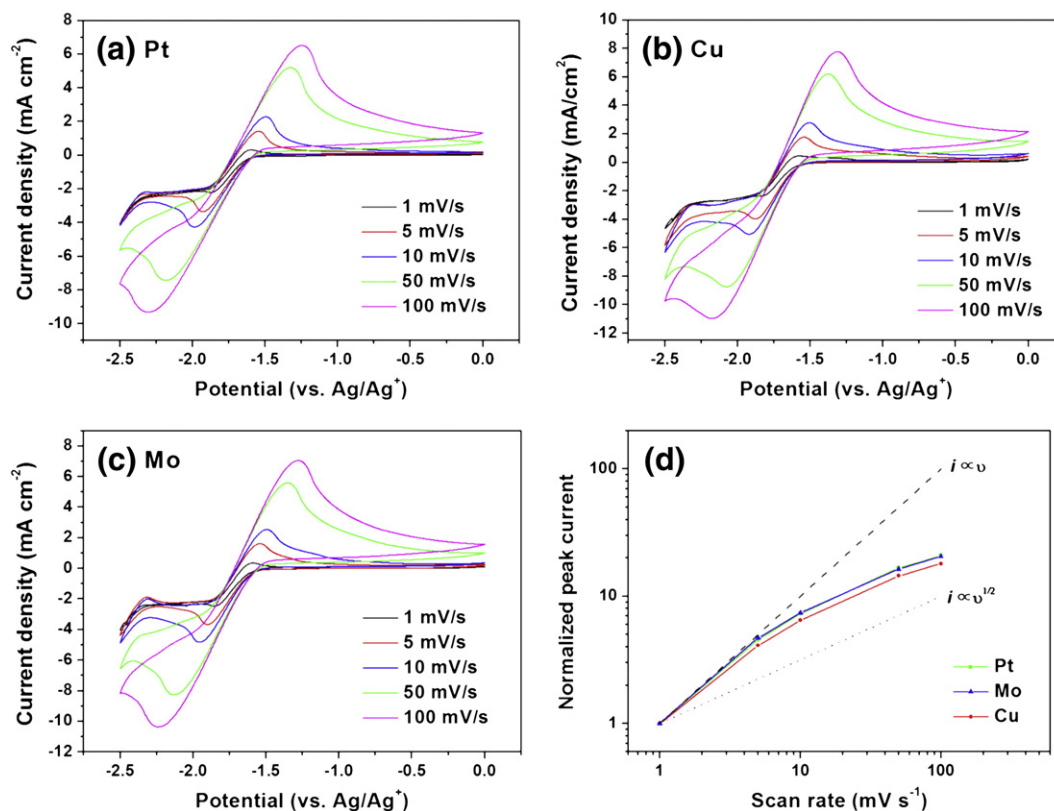

Fig. 2. Cyclic voltammograms of (a) Pt, (b) Cu, and (c) Mo for the $[Ni(bpy)_3]/[Ni(bpy)_3]^{2+}$ couple at various scan rates and (d) normalized anodic peak current as a function of the scan rate.
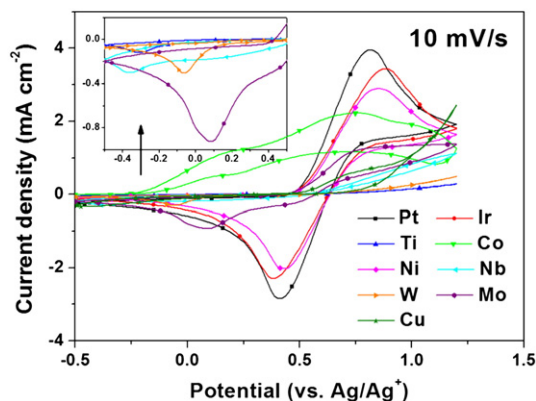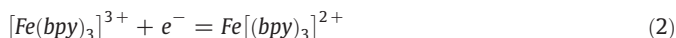
Fig. 3. Cyclic voltammograms of various metal electrodes for the $[Fe(bpy)_3]^{2+}/[Fe(bpy)_3]^{3+}$ couple at a scan rate of 10 mV s^{-1}.

of $[Fe(bpy)_3]^{2+}/[Fe(bpy)_3]^{3+}$ couple which was reported in the literature as the following reaction [7]:

$$[Fe(bpy)_3]^{3+} + e^- = Fe[(bpy)_3]^{2+} \qquad (2)$$

The cathodic peak current densities range between 2 and 3 mA cm^{-2} and the shapes of the CVs are quite symmetric, implying good reversibility of the redox reaction. The second group is comprised of Mo, W, Nb, and Ti metals, the enlarged CVs of which are displayed in the inset graph of Fig. 3. These electrodes produced more overpotential and the current densities are lower than 1 mA cm^{-2}, which means the kinetics of the redox reaction on the electrodes is relatively sluggish. And the third group consists of Cu and Co. On these electrodes, the characteristic cathodic peak is not observed, indicating that they are not suitable for the reversible redox reaction. On the basis of the analysis of the CV curves, it is noteworthy that the reactivity of metal complexes strongly depends on the type of metal electrodes.

To compare the rate performances of Pt, Ir, and Ni electrodes for the $[Fe(bpy)_3]^{2+}/[Fe(bpy)_3]^{3+}$ redox couple, the CV curves at scan rates ranging from 1 to 100 mV s^{-1} are shown in Fig. 4. It can be also seen that the voltage separation between cathodic and anodic current peaks increases with increasing the scan rate. The cathodic peak current of the metal electrodes is plotted as a function of the scan rate in Fig. 4(d). Similarly to the metal electrodes for the Ni bipyridine couple, all electrodes initially show the linear dependence and begin to deviate from it at one point. Over the entire range of scan rates, Ni shows relatively better rate performance. For the $[Fe(bpy)_3]^{2+}/[Fe(bpy)_3]^{3+}$ couple, Ni is found to be the best candidate among non-precious metals in terms of cathodic peak current value at a fixed scan rate and rate capability.

A non-aqueous RFB is constructed of Mo (or Cu) as a negative electrode for the anolyte including the Ni bipyridine couple and Ni as a positive electrode for the catholyte including the Fe bipyridine couple. The CV curves of the Mo electrode for the $[Ni(bpy)_3]/[Ni(bpy)_3]^{2+}$ couple and the Ni electrode for the $[Fe(bpy)_3]^{2+}/[Fe(bpy)_3]^{3+}$ couple are combined in Fig. 5. The operation voltage of the battery is expected to be ca. 1.9 V, which is estimated from the voltage difference of the peak current positions. In comparison to the Pt electrode, it is concluded that some non-precious metals for each metal complex redox couple have a potential as electrodes for non-aqueous RFBs. Further studies on surface area effect and durability of metal electrodes are now in progress.
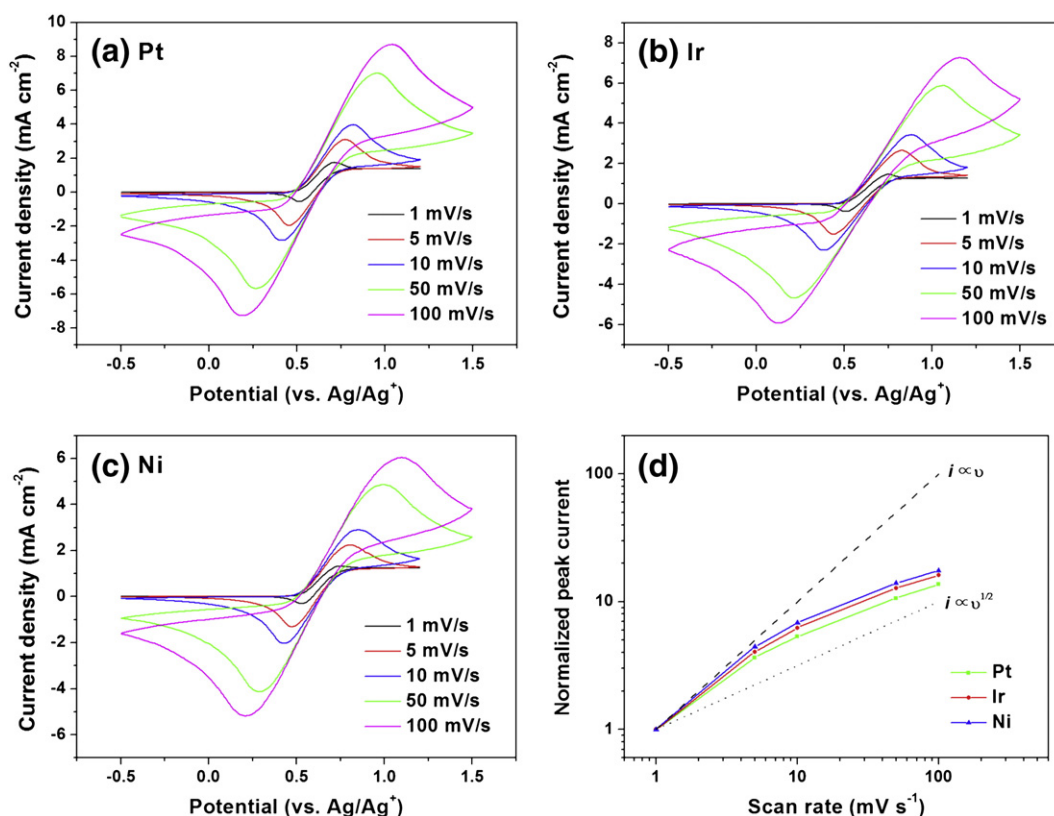

Fig. 4. Cyclic voltammograms of (a) Pt, (b) Ir, and (c) Ni for the $[Fe(bpy)_3]^2/[Fe(bpy)_3]^{3+}$ couple at various scan rates and (d) normalized cathodic peak current as a function of the scan rate.
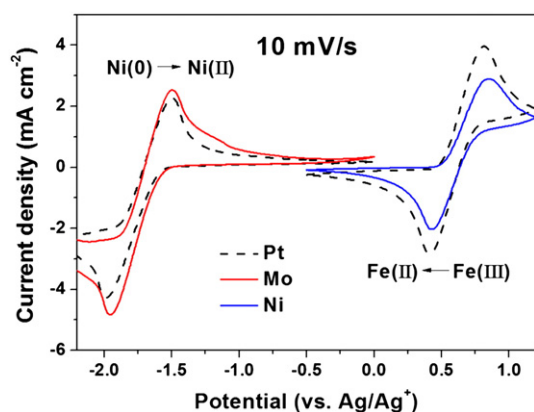
Fig. 5. Cyclic voltammograms of Mo for the $[Ni(bpy)_3]/[Ni(bpy)_3]^{2+}$ couple and Ni for the $[Fe(bpy)_3]^{2+}/[Fe(bpy)_3]^{3+}$ couple. The CVs of Pt for both couples were included for comparison.

4. Conclusions

Various metal electrodes were examined for Ni(0)/Ni(II) and Fe(II)/Fe(III) redox couples using cyclic voltammetry. On the basis of the analysis of the CVs, the reactivity and kinetics for the electrochemical reactions of metal complexes were found to strongly depend on the type of metal electrodes. Among non-precious metals, Cu and Mo presented relatively better electrocatalytic activities as negative electrodes for the Ni(0)/Ni(II) redox couple and Ni appeared to be the best material as a positive electrode for the Fe(II)/Fe(III) redox couple in terms of electrochemical reactivity and kinetics.

Acknowledgement

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